Electronic Supplementary information for 'A plutonium-based single-molecule magnet'

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1. Synthesis

The solvents were purchased from Aldrich in their anhydrous form conditioned under argon. The potassium salt of the ligand (KTp) was prepared as previously described.[S1] The room-temperature reaction of 1 equiv. of $PuCl_3$ with 3.05 equivalents of KTp in water leads to the precipitation of $PuTp_3$. Purification proceeds via washing with water, ethanol, and diethylether and drying of the residue. Extraction with benzene yields in 90 % of single crystalline material. Elemental analysis (%) calculated for $^{239}PuTp_3$ ($B_3C_{27}H_{30}N_{18}Pu$; 878.069 g/mol) C 36.97; H 3.45; N 28.74; Pu 27.21. Found Pu 27.5.

2. Spectroscopic data

FTIR and Solid state UV-NIR spectra were recorded respectively on a Perkin-Elmer 2000 IR-spectrometer and on a Perkin-Elmer Lambda 9 spectrometer. The observed transitions are listed in the following.

IR (KBr; cm^{-1}): 3142(m), 3119(w), 3112(w), 2453(sh), 2442(s), 2405(m), 2374(w), 1505(s), 1431(m), 1423(m), 1406(s), 1381(s), 1301(vs), 1293(vs), 1226(m), 1212(vs), 1197(m), 1185(m), 1129(m), 1121(vs), 1085(w), 1061(m), 1048(vs), 974(vs), 924(w), 920(w), 899(w), 878(w), 804(w), 777(m), 769(vs), 750(vs), 739(m), 725(vs), 670(m), 625(m), 620(m)

FIR (Polyethylen; cm^{-1}): 338(m), 332(m), 319(m), 260(w), 182(m), 161(m), 136(vs)

(w = weak, m = medium, s = strong, vs = very strong)

Solid state UV-NIR spectrum taken on a Perkin-Elmer Lambda 9 spectrometer.

NIR/VIS (KBr; nm): 1556, 1413, 1189, 1147, 1100, 1049, 1023, 928, 912, 822, 814, 805, 796, 774, 768, 669, 605, 565, 511.

3. X-Ray Crystallography

Diffraction data were measured at 100 K on a Bruker APEX II Quazar diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å) in the Ω-range from 1.48 to 28.452°. 2844 frames were collected with an irradiation time of 3 s per frame obtained from eight runs performed with ϕ- or ω-scans with $\Delta\omega = \Delta\phi = 0.5°$. The data were integrated with SAINT[S2] and corrected to Lorentz and polarisation effects; absorption effects were corrected with SADABS.[S3] The structure was solved by direct methods and refined to an optimum R_1 value with SHELXL-2013.[S4] Visual evaluation was performed with XPMA.[S5] Refinement of F^2 proceeded against all reflections. Data have been deposited at the CCDC with the reference number 994710, and are available on request from http://www.ccdc.cam.ac.uk/.

Table S1. Crystallographic data.

Empirical formula	$B_3C_{27}H_{30}N_{18}Pu$
Formula weight	878.09
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	P 63/m
Unit cell dimensions	a = 11.7036(5) Å
	c = 13.5561(8) Å
Volume	1608.07(17) $Å^3$
Z	2
Density (calculated)	1.814 Mg/m^3
Absorption coefficient	2.102 mm^{-1}
F(000)	854
Crystal size	0.118 x 0.068 x 0.064 mm^3
Ω range for data collection	2.009 to 28.452°
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-18 \le l \le 17$
Reflections collected	28954
Independent reflections	1381 [R(int) = 0.0502]
Completeness to theta = 25.000°	99.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.922 and 0.862
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1381 / 0 / 108
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	$R_1 = 0.0149$, $wR_2 = 0.0311$
R indices (all data)	$R_1 = 0.0178$, $wR_2 = 0.0318$
Largest diff. peak and hole	0.593 and -0.661 $eÅ^{-3}$

Table S2. Bond lengths [Å] and angles [°].*

Pu(1)-N(1)	2.5883(15)
Pu(1)-N(3)	2.762(2)
N(1)-C(1)	1.336(2)
N(1)-N(2)	1.373(2)
N(2)-C(3)	1.351(2)
N(2)-B(1)	1.544(2)
N(3)-C(4)	1.338(3)
N(3)-N(4)	1.369(3)
N(4)-C(6)	1.342(3)
N(4)-B(1)	1.530(4)
C(1)-C(2)	1.389(3)
C(2)-C(3)	1.372(3)
C(4)-C(5)	1.400(4)
C(5)-C(6)	1.370(4)
B(1)-N(2)#1	1.544(2)
N(1)#1-Pu(1)-N(1)#2	84.13(5)
N(1)#1-Pu(1)-N(1)#3	134.49(2)
N(1)#2-Pu(1)-N(1)#3	78.64(7)
N(1)#1-Pu(1)-N(3)#4	67.53(4)
N(1)#2-Pu(1)-N(3)#4	140.68(3)
N(1)#4-Pu(1)-N(3)#4	66.96(4)
N(3)#4-Pu(1)-N(3)	120.0
C(1)-N(1)-N(2)	105.62(15)
C(1)-N(1)-Pu(1)	129.29(12)
N(2)-N(1)-Pu(1)	123.64(11)
C(3)-N(2)-N(1)	109.44(15)
C(3)-N(2)-B(1)	127.25(17)
N(1)-N(2)-B(1)	123.15(16)
C(4)-N(3)-N(4)	105.1(2)
C(4)-N(3)-Pu(1)	132.14(17)
N(4)-N(3)-Pu(1)	122.72(15)
C(6)-N(4)-N(3)	110.7(2)
C(6)-N(4)-B(1)	128.4(2)
N(3)-N(4)-B(1)	120.8(2)
N(1)-C(1)-C(2)	111.55(17)
C(3)-C(2)-C(1)	104.45(17)
N(2)-C(3)-C(2)	108.94(17)
N(3)-C(4)-C(5)	111.1(2)
C(6)-C(5)-C(4)	104.7(2)
N(4)-C(6)-C(5)	108.3(2)
N(4)-B(1)-N(2)	108.41(14)
N(2)#1-B(1)-N(2)	112.5(2)

* Symmetry transformations used to generate equivalent atoms:
#1 x,y,-z+3/2 ; #2 -y+1,x-y+1,-z+3/2 ; #3 -y+1,x-y+1,z; #4 -x+y,-x+1,z
Unlisted distances or angles are identical to ones already present in the table.

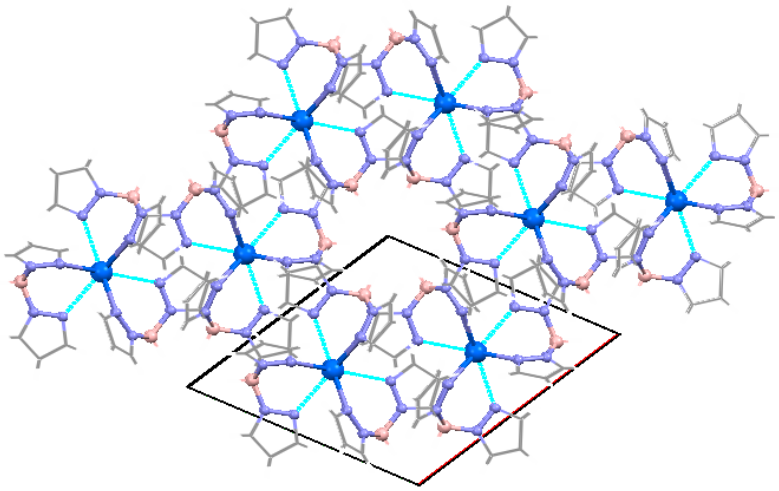

Figure S1. Cell packing along the c axis of $PuTp_3$. Plutonium atoms are shown in blue, nitrogen in violet, and boron ions are shown in pink.

4. *M*agnetic characterization

The temperature-dependent *dc* magnetic susceptibility has been measured in the temperature range from 1.9 to 300 K with a Quantum Design MPMS-7T Superconducting Quantum Interference Devices (SQUID). Susceptibility data have been collected with applied magnetic fields $\mu_0 H$ ranging from 0.05 to 7 T on a sample of 58.15 mg using compressed powder in a Suprasil-Quartz sample holder. The sample was restrained to prevent grain torqueing using a fitted quartz stopper, and was sealed under argon before measurement. The contribution to the signal of the empty sample holder was measured before the encapsulation and subtracted from the total signal. The susceptibility has been obtained as the ratio between the longitudinal magnetization and the applied magnetic field. The resulting data were corrected for the diamagnetic contribution using tabulated Pascal's constants. Magnetic calibration was done with a cylindrical palladium standard having approximately the same geometry of the measured samples.

The real and imaginary parts of the *ac* magnetic susceptibility were measured as a function of temperature on the same sample using a Quantum Design PPMS-14T platform; data for this experiment were collected on warming from 1.9 to 40 K, after zero-field cooling of the sample. For each run of measurements, the excitation a.c. field was applied with a fixed amplitude of $\mu_0 H_{ac}$ = 10 G and fixed frequencies f, ranging from 18 to 9987 Hz. The temperature of the samples was controlled with an accuracy of about 0.1 K.

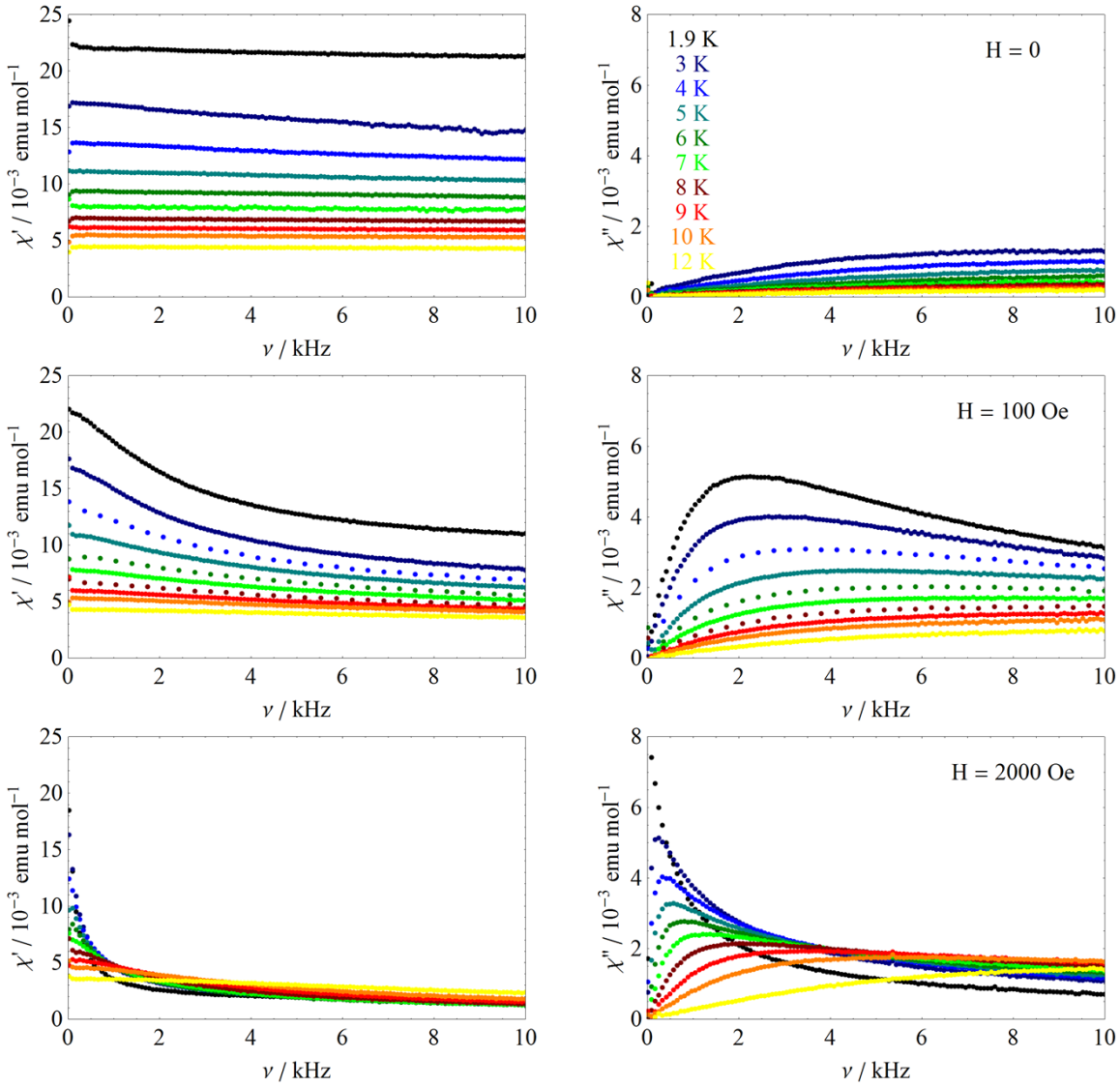

Figure S2. Frequency dependence of the a.c. magnetic susceptibility measured for $PuTp_3$ at various temperature and field values (see text for details).

Isotherms of the frequency dependent a.c. magnetic susceptibility have also been measured at several temperatures from 1.9 to 12 K in the frequency range from 18 Hz to about 10 kHz, both with and without a superimposed field ($\mu_0 H_{dc}$ = 0, 100 Oe, 2000 Oe), generated by a superconducting d.c. magnet. The results obtained with field $\mu_0 H_{dc}$ = 100 Oe have been fitted to a modified Debye relaxation law valid in the low frequency range and allowing for a continuous distribution of the relaxation time τ:[S6]

$$\chi_{ac}(\omega) = \chi_S + \frac{\chi_T - \chi_S}{1 + (i\omega\tau_c)^{1-\alpha}} \qquad \text{S1}$$

Where χ_T is the isothermal susceptibility in the limit $\omega\tau << 1$, $\chi_S = \chi_{ac}(\infty)$ is the adiabatic susceptibility, $\omega = 2\pi f$ is the angular frequency and τ_c is the average relaxation time. The

parameter α determines the width of the time relaxation distribution function g(lnτ). Equation S1 can be separated into real and imaginary components corresponding to the in-phase and out-of-phase susceptibilities

$$\chi'_{ac}(\omega) = \chi_S + \frac{\chi_T - \chi_S}{2}\left(1 - \frac{\sinh[(1-\alpha)\ln(\omega\tau_c)]}{\cosh[(1-\alpha)\ln(\omega\tau_c)] + \sin(\alpha\pi/2)}\right) \quad \text{S2}$$

and

$$\chi''_{ac}(\omega) = \frac{\chi_T - \chi_S}{2}\left(\frac{\cos(\alpha\pi/2)}{\cosh[(1-\alpha)\ln(\omega\tau_c)] + \sin(\alpha\pi/2)}\right). \quad \text{S3}$$

Table S3. Parameters obtained by fitting Cole-Cole plots to the modified Debye relaxation model.

T (K)	χ_S (10^{-3} emu/mol)	χ_T (10^{-3} emu/mol)	τ_c (μs)	α
1.9	9.12	22.34	66.4	0.166
3.0	6.20	17.09	56.5	0.175
4.0	4.86	13.69	43.9	0.214
5.0	3.57	11.45	30.4	0.283
6.0	2.16	9.40	17.6	0.334
7.0	1.36	8.16	11.9	0.368
8.0	0.63	7.12	7.82	0.405
9.0	0.32	6.34	5.56	0.416
10.0	0.04	5.47	3.92	0.368
12.0	0.05	4.42	2.65	0.341

The parameters obtained from the fits are reported in Table S3, and the corresponding distribution function for the relaxation times on a logarithmic scale is given by

$$g(\ln\tau) = \frac{1}{2\pi}\left(\frac{\sin(\alpha\pi)}{\cosh[(1-\alpha)\ln(\tau/\tau_c)] - \cos(\alpha\pi)}\right). \quad \text{S4}$$

As an example, the g(lnτ) distribution obtained at 1.9 and 12 K are shown in the inset of Fig. 4. The α parameter increases with increasing temperature, thus the distribution function g(lnτ) becomes progressively broader.

5. Additional references

[S1] a) S. Trofimenko, *J. Am. Chem. Soc.* **1967**, *89,* 3165; b) S. Trofimenko, *Inorg. Synth.* **1970**, *12*, 99.

[S2] SAINT: Bruker **2007**, Bruker AXS Inc., Madison, Wisconsin, USA.

[S3] SADABS: Bruker **2007**, Bruker AXS Inc., Madison, Wisconsin, USA.

[S4] SHELXL-2013: G. M. Sheldrick, **2013**, University of Göttingen, Germany.

[S5] XPMA: L. Zsolnai, **1997**, University of Heidelberg, Germany.

[S6] a) D. Huser, A. J. Vanduyneveldt, G. J. Nieuwenhuys, J. A. Mydosh, *J. Phys. C: Solid State Phys.* **1986**, *19*, 3697; b) U. T. Hochli, *Phys. Rev. Lett.* **1982**, *48*, 1494.